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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Stuart, M. C. A., Scarzello, M., Klijn, J. E., Boekema, E. J., & Engberts, J. B. F. N. (2008). *Self assembly and phase behaviour of new sugar based gemini amphiphiles*. 49-50. Abstract from 14th European Microscopy Congress 1–5 September 2008, Aachen, Germany.

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Self assembly and phase behaviour of new sugar based gemini amphiphiles

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Keywords: cryo-electron microscopy, phase behaviour, gemini surfactant.

Amphiphilic molecules possess parts which are distinctively hydrophobic and other parts which are distinctively hydrophilic. This ambivalence lies at the basis of the intriguing properties of these molecules, selected by nature as the building-blocks of architectures essential for life. Amphiphile self-assembly can lead to a variety of structures, differing in shape and size, depending on the molecular structure of the amphiphile and on the solution conditions such as temperature, ionic strength and pH. A relatively new and particularly interesting class of amphiphilic molecules, the gemini surfactants (GS), is obtained by connecting two single-tailed surfactants via a spacer at the level of the headgroups. The sugar-based gemini surfactant consists of several unique structural elements by which self-assembly properties can be made to fit the desired properties. The tertiary amino moieties in the headgroup can be protonated depending on the solution pH. The reduced sugars can be varied in length and stereochemistry. The spacer is either hydrophobic or hydrophilic and can be varied in length and the hydrophobic alkyl chain can be varied in length and degree of saturation. Most gemini surfactants form vesicles around neutral pH and exhibit a phase change towards micelles upon decreasing the pH, figure 1. When the nitrogens are protonated the cross-sectional headgroup area increases which gives the molecule a cone-shape appearance. The pH at which the phase changes from lamellar to micellar is dependent on the spacer length [1]. The shorter the spacer the more difficult it is to protonate both nitrogens which gives a lower pH of transition. At high pH the vesicles become neutral which leads to a decreased colloidal stability and the vesicles aggregated. Surprisingly the vesicles redispersed upon a further increase of the pH which could only be explained by OH⁻ binding to the vesicle surface giving the vesicle a negative ζ potential. The pH at which vesicle redispersion starts was found to be correlated with the sugar stereochemistry [2].

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2. J. E. Klijn, M. C. A. Stuart, M. Scarzello, A. Wagenaar, and J. B. F. N. Engberts. *J.Phys.Chem.B.* **111** (2007), 5204.

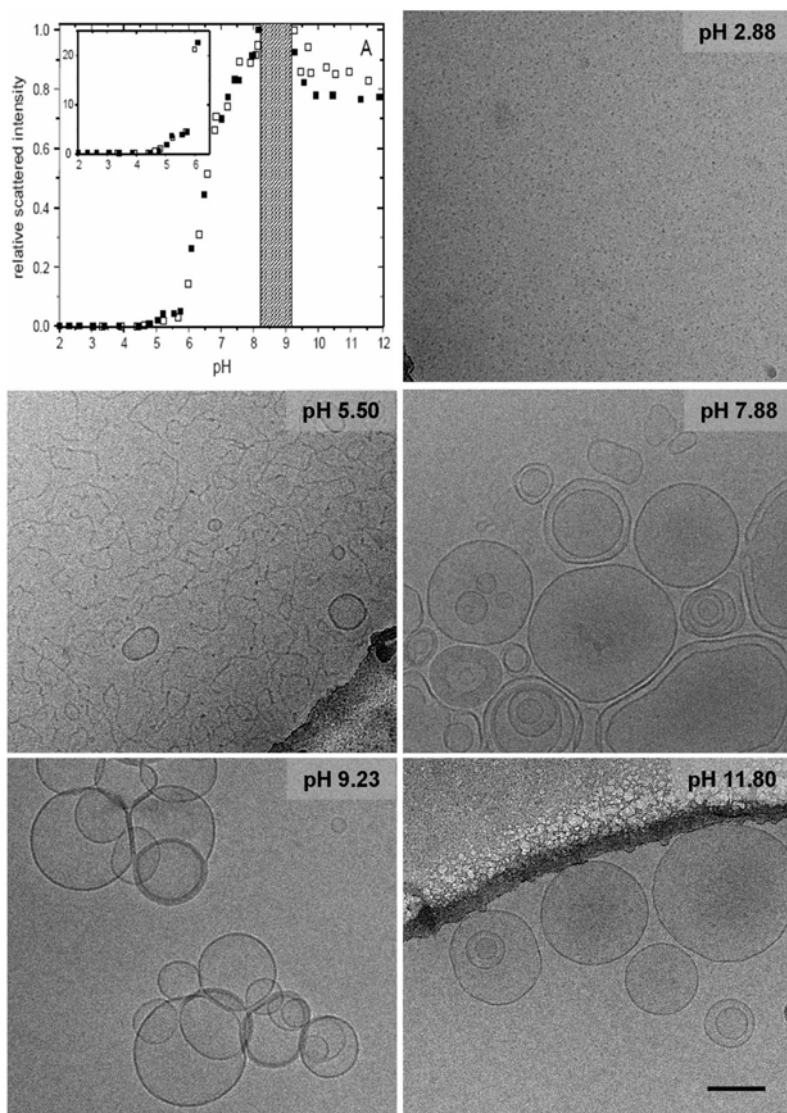


Figure 1. pH depended phase and aggregation behaviour of reduced glucose gemini surfactant with C6 spacer and oleoyl tails followed with dynamic light scattering and cryo-electron microscopy. At low pH micelles are formed. At somewhat higher pH the micelles aggregate into worm-like micelles. At neutral pH and above vesicles are formed. Between pH 8.2 and 9.3 the vesicles aggregate due to charge neutralization. At high pH the vesicles redisperse as the result of OH^- binding to the vesicle surface. Bar 100 nm.